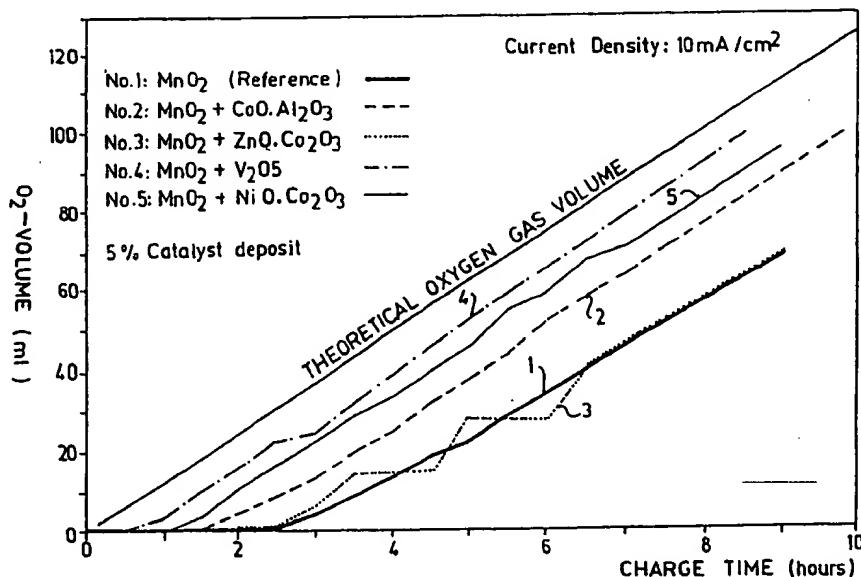




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: **MANGANESE DIOXIDE CATHODE FOR RECHARGEABLE ALKALINE MANGANESE DIOXIDE CELLS WITH IMPROVED OVERCHARGE PROPERTIES**



## (57) Abstract

Manganese dioxide cathode for rechargeable alkaline manganese dioxide cells with improved overcharge properties, which in addition to conventional components comprises at most 10 mass% catalyst, making the oxygen evolution during overcharge stoichiometrically equivalent to the charge current without the side reaction to the manganate. The applicable catalysts (alone or in combination) are members of the following group: CoAl<sub>2</sub>O<sub>4</sub> (= CoO.Al<sub>2</sub>O<sub>3</sub>), ZnCo<sub>2</sub>O<sub>4</sub> (= ZnO.Co<sub>2</sub>O<sub>3</sub>), NiCo<sub>2</sub>O<sub>4</sub> (= NiO.Co<sub>2</sub>O<sub>3</sub>), V<sub>2</sub>O<sub>5</sub>, NiO, Co<sub>3</sub>O<sub>4</sub>, Ni<sub>0.2</sub>CoO.

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MANGANESE DIOXIDE CATHODE FOR RECHARGEABLE  
ALKALINE MANGANESE DIOXIDE CELLS WITH  
IMPROVED OVERCHARGE PROPERTIES

TECHNICAL FIELD:

The present invention relates to a manganese dioxide cathode for rechargeable alkaline manganese dioxide cells with improved overcharge properties, more particularly to catalysts added to the conventional manganese dioxide cathode material which substantially improve the overcharge properties of the cell.

BACKGROUND OF THE INVENTION:

The oxygen overcharge principle is well known from the nickel-cadmium batteries. The imbalance of the electrode capacities is essential, in order to assure that the cathode reaches the fully charged state first. This is achieved by there being still CdO left in the anode when the nickel oxide is starting to evolve oxygen gas. The oxygen then travels to the anode and recombines with the metallic cadmium. In nickel oxide -- hydrogen cells the liberated oxygen reacts with the hydrogen gas in a catalytic reaction supported by the surface of the fuel cell type anode and forms water. Due to the fact that this is a closed cycle in a gas-tight sealed cell, the overall electrolyte concentration does not change and the only product of the overcharge reaction is heat.

When manganese dioxide is charged beyond the fully charged state -- which is not well defined -- not only oxygen gas but also soluble (VI-valent) manganate is formed. The oxygen gas can then react with hydrogen, cadmium or zinc. However, the manganate disproportionates to IV-valent manganese dioxide (which can be discharged and charged again) and II-valent manganese compounds which are not rechargeable. A rough estimate shows that a loss of only 1% in rechargeable  $\text{MnO}_2$  per cycle results in a 50% loss of capacity over 50 cycles. In reality, the efficiency of charging is poor during the first cycles and levels off to better values later. It was also found that adding titanium salts improved the cycling efficiency. This is discussed in German Patent DE 33 37 568 C2.

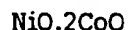
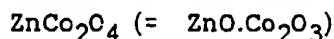
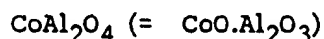
It was found that simply adding about 20% nickel oxide to the manganese dioxide induced earlier oxygen evolution, before manganates were formed. This is discussed in U.S. patent 3,288,642. However, this effect was lost after repeated cycling, when the higher nickel oxides were formed and the oxygen evolution potential was rising above the (fully charged)  $\text{MnO}_2$  potential (1.75 V against zinc).

Owing to the formation of manganates during overcharge which substantially reduces the useful capacity of the cells, the charging of alkaline manganese dioxide cells requires specific methods in which the value of the charging voltage should be kept below 1.72 to 1.75 V. This requirement increases charging time, makes the electronic monitoring of the charged state of the cell difficult and requires the use of specific charger circuits which are more expensive than conventional ones that are used in large scale for nickel cadmium batteries.

The object of the invention is to provide a manganese dioxide cathode material which has improved overcharge properties, which enables the use of chargers with operational voltage above 1.75 V, in which the formation of manganates is effectively prevented during overcharge, whereby there will be a smaller decrease in capacity during cycle life, and in which the end of charge state can be monitored more easily.

It has been found according to the present invention that the addition of certain catalysts to the conventional manganese dioxide cathode material can make the oxygen evolution stoichiometrically equivalent to the charge current without the side reaction to the manganate. These catalysts do not lose the oxygen overvoltage but suppress the formation of manganate nearly one hundred percent effectively until the normal oxygen evolution voltage (1.9 V) is reached. These catalysts react reversibly on charge and discharge at 10 to 15  $\text{mA/cm}^2$  current density.

It has been found that such catalysts can be any of the following oxides when used in an amount up to 10 mass% compared to the cathode mass:



In a preferable embodiment the amount of said catalysts lies between 1 and 5 mass%.

The use of nickel oxide in an amount of at most 5 mass%, preferably 1 to 3 mass%, in combination with either one of vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) or nickel cobaltite ( $\text{NiO} \cdot \text{Co}_2\text{O}_3$ ) is preferable, due to improved potential characteristics in the overcharge region.

The use of these catalysts (dopants) results in a quantitative conversion of input charges to oxygen. The catalyst acts without heat treatment of the mixture, and thus practically excludes the possibility of introducing ions in the  $\text{MnO}_2$  lattice. The effect of vanadium pentoxide over a longer period of time might be questionable, because of its solubility in alkali hydroxides. The nickel cobaltite is very poorly soluble even in strong acids and bases. This is therefore a more preferable choice.

These catalysts are active at currents far higher than those normally observed on cells under overcharge conditions. A constant voltage charger supplies only fractions of the tested current densities at the end of charge. Under such circumstances the potential of the electrode is not shifted significantly and the stability of the catalyst is not a limited factor.

Although the tests were carried out with a maximum amount of 5% of the catalysts, it can well be seen that an increase of the amount of the catalysts does not change the cathode performance. The increased use of such materials is disadvantageous in the sense that they occupy the space of the useful manganese dioxide cathode material. There is therefore no sense of using more than about 5 to 10 mass% of these catalysts.

The substantially improved overcharge properties of manganese dioxide cathodes that are achieved according to this invention can be utilized in all types of rechargeable cells using manganese dioxide as the cathode electrode. It must be understood, however, that in the overcharge mode, oxygen gas is developed and the cell design should provide a reaction (recombination) for this oxygen gas. This constitutes no problems for a number of cell types, while in other cells specific measures should be introduced for this purpose.

Owing to the use of these catalysts, the overcharge potential curves will be changed in such a way that a well-detectable voltage increase is obtained in the overcharge period which can be used to trigger an end of charge signal before irreversible cathode reactions could start. This behavior enables the use of conventional or at least less precise charger circuits, since there will be no need to inhibit the increase of the charging voltage above 1.75 V.

#### BRIEF DESCRIPTION OF THE DRAWINGS:

The invention will now be described in connection with preferable embodiments and examples, wherein reference will be made to the accompanying drawings. In the drawing:

Figure 1 shows the schematic arrangement of a test cell;

Figure 2 shows the basic measuring arrangement;

Figure 3 comprises oxygen evolution verses time diagrams for difficult catalysts;

Figure 4 shows potential curves for the catalysts of FIG. 3;

Figure 5 shows oxygen evolution curves: the catalyst is  $V_2O_5$ ;

Figure 6 shows potential curves: the catalyst is  $V_2O_5$ ;

Figure 7 shows oxygen evolution curves: the catalyst is  $NiO.Co_2O_3$ ;

Figure 8 shows potential curves: the catalyst is  $NiO.Co_2O_3$ ;

Figure 9 shows oxygen evolution curves in a charge-discharge cycle: the catalyst is 5%  $NiO.Co_2O_3$ , and current density is 10 mA/cm<sup>2</sup>

Figure 10 is similar to Figure 9 but with a 7.5 mA/cm<sup>2</sup> current density; and

Figure 11 shows potential curves compared to a zinc reference, for the tests of Figs. 9 and 10.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS:**

The experiments illustrating the various effects of the present invention were made by using manganese dioxide cathodes. These cathodes were made in a conventional manner, with the exception that a variety of catalysts were added to the starting mix of the cathode material.

To this end, before making the different types of manganese dioxide cathodes, the following catalysts were obtained:

- i)  $\text{CoAl}_2\text{O}_4$  (=  $\text{CoO} \cdot \text{Al}_2\text{O}_3$ )
- ii)  $\text{ZnCo}_2\text{O}_4$  (=  $\text{ZnO} \cdot \text{Co}_2\text{O}_3$ )
- iii)  $\text{NiCo}_2\text{O}_4$  (=  $\text{NiO} \cdot \text{Co}_2\text{O}_3$ )
- iv)  $\text{V}_2\text{O}_5$

Except for the vanadium pentoxide, which was available in reagent grade purity (MERCK No. 824), the required compounds were prepared by mixing aqueous solutions containing the nitrates of the oxide forming metals in stoichiometric ratio, evaporizing the water and heating the residue for at least 3 hours at a temperature of 850 °C in the presence of air. The product were tested by X-ray inspection.

Manganese dioxide electrodes were prepared by using the following materials:

- a) electrolytic manganese dioxide, Mitsui, IBA sample No. 18
- b) graphite power, Lonza, KS 44, IC-sample No. 1
- c) Hostaflon powder, Hoechst, PTFE 2071.

The basic mixture was 82 mass% of electrolytic manganese dioxide, 10 mass% of graphite, and 8 mass% of Hostafion. After dry mixing these components, the powder obtained was immersed in benzene (boiling range 80-110 °C) and homogenized for 3-4 hours. Subsequently the excess benzene was separated by filtration and the solid residue was kneaded until the paste had a suitable consistency for the following rolling process. Rolling started with a sheet of

about 4mm thickness and was continued step by step until a final thickness of 0.8 to 0.9 mm was achieved. In the last step the foil was rolled on a nickel screen used as a current collector. Finally, the product was dried at 40 °C for 12 hours. Circular electrodes with a diameter of 50.2 mm were cut out, contacted with a nickel wire and used as working electrodes in the test cell.

Further cathode electrodes were made by adding 1 to 5 mass% amount of the above listed catalysts i) to iv) before the dry mixing step.

The test cell was made as illustrated in Fig. 1. A pair of polymetacrylate plates 1, 2 were used which could be fitted by four bolts (not shown). Appropriate recesses were provided on the plates to give space to a circular electrode and to the electrolyte. Plate 2, which received the working electrode 3 (i.e. the manganese dioxide cathode with the catalyst under test), was fitted with a tube system 4 for gas collection. A separator sheet 5 was placed between the two plates 1, 2. In the recess of the other plate 1, a counter electrode 6 made by a nickel screen and a reference electrode 7 formed by a zinc wire were placed in a spaced geometry, and the so obtained compartment was vented to let the produced hydrogen escape. On the other side, the evolved oxygen was collected and its volume was recorded.

After fixing the electrodes, the compartments were filled with 9 molar KOH, the plates were fitted together, and sealed in an airtight way. The working and counter electrodes 3 and 6 were connected to a galvanostat 10 and a potential recorder 11 was coupled to the working and reference electrodes 6, 7 (Fig. 2). The evolved oxygen volume was measured by meter 12.

The working electrodes were applied in 90 to 95 % charged condition (as they were produced), and this means that the overcharge reactions started nearly as soon as the cell was powered by the galvanostat.



The tests were performed with cathode samples from the various catalyst types and amounts; as well as with a conventional manganese dioxide cathode without and catalyst, as standard.

In the ideal case (efficient catalyst additive), the oxygen evolution curve followed the pre-calculated track with practically identical slope. Only a small number of tests included a discharge period of the working electrode to detect possible changes in its performance.

The first series of experiments was started to establish the properties of an undoped  $\text{MnO}_2$  electrode comparing it with electrodes containing 5 mass% of doping oxide. As Fig. 3 shows, the amount of evolved oxygen is significantly different and clearly depending on the nature of the added oxide. The only exception is found in curve 3 (zinc-cobaltite  $\text{ZnO} \cdot \text{Co}_2\text{O}_3$  which is close to curve 1 (undoped  $\text{MnO}_2$ ), and shows no advantage of this additive. The overcharge experiments were carried out by applying constant current densities between 3  $\text{mA}/\text{cm}^2$ . The straight line shows the theoretic oxygen gas volume.

The voltage versus time curves shown in Fig. 4 indicate that -- besides the irregular performance of zinc-cobaltite -- a plateau is achieved in all cases and is situated slightly above the curve of pure  $\text{MnO}_2$ .

The most promising results of this first series of tests were given by the vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) and by the nickel cobaltite ( $\text{NiO} \cdot \text{Co}_2\text{O}_3$ ). Consequently, the following experiments should determine if lower concentrations of the doping oxide were able to give similar results. The result for different amounts of vanadium pentoxide are summarized in Figs. 5 and 6. In these diagrams, the correlation between the percentage  $\text{V}_2\text{O}_5$  content and the experiment number, is as follows:

- # 6 corresponds to 5 %  $\text{V}_2\text{O}_5$
- # 9 corresponds to 3 %  $\text{V}_2\text{O}_5$
- # 8 corresponds to 1 %  $\text{V}_2\text{O}_5$

The amount of evolved oxygen at a given time is clearly dependent on the concentration of the additive, but the effect -- as indicated by the identical slope -- is visibly the same. The correlation between the concentration of the added oxide and the level of the potential plateau (Fig. 6) seems to be regular: the higher the amount of vanadium oxide in the electrode, the higher is the potential in the steady state.

Similar tests were made in case of different amounts of  $\text{NiO} \cdot \text{Co}_2\text{O}_3$  which can be seen in Figs. 7 and 8. The correspondence table is as follows:

- # 7 corresponds to 5%  $\text{NiO} \cdot \text{Co}_2\text{O}_3$
- # 10 corresponds to 3%  $\text{NiO} \cdot \text{Co}_2\text{O}_3$
- # 11 corresponds to 1%  $\text{NiO} \cdot \text{Co}_2\text{O}_3$

In the case of nickel cobaltite, the correlation of the results is not so evident. Fig. 7 demonstrates that the extent of the oxygen evolution is nearly not determined by the amount of additive. 1% of nickel cobaltite gives the same result as 5% and it is possible that even contents below 1% will be active. The potential versus time functions shown in Fig. 8 point out that there seems to be an optimum at a concentration of 3%, which was the least effective from the point of view of oxygen evolution.

Another point to be cleared up was the performance of doped electrodes after a period of discharge. For this reason, two electrodes containing 5% of nickel cobaltite were prepared and one was discharged for 1 hour with a current density of 10  $\text{mA/cm}^2$  and thereafter switched to charge. The other one was discharged for 2 hours at 7.5  $\text{mA/cm}^2$  and then reversed at the same current density. The performance can be seen in Figs. 9 and 10, wherein:

Fig. 9:

- # 7 shows a fully charged electrode, 5%  $\text{NiO} \cdot \text{Co}_2\text{O}_3$  doped
- # 13 shows a 1 hour predischarged electrode, 5%  $\text{NiO} \cdot \text{Co}_2\text{O}_3$  doped current density: 10  $\text{mA/cm}^2$

Fig. 10:

# 5 shows a fully charged electrode, 5%  $\text{NiO} \cdot \text{Co}_2\text{O}_3$  doped

# 12 shows a 2 hours predischarged electrode, 5%  $\text{NiO} \cdot \text{Co}_2\text{O}_3$   
doped current density:  $7.5 \text{ mA/cm}^2$

The results obtained in both diagrams were compared to adequate experiments with fully charged electrodes. It is apparent that the slope of the curves remains unchanged, and only the time-lag before the gassing starts is extended. The recorded potentials show clearly the periods of discharge and subsequent charge (Fig. 11). The higher value for # 13 is due to the higher current density.

Further tests were carried out to determine the coulombic efficiency in cases, of different catalysts with differing concentration. The coulombic efficiency characterizes the oxygen evolution reaction after reaching the voltage plateau. The data are summarized in Table 1:

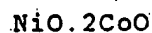
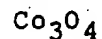
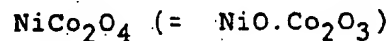
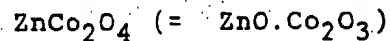
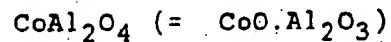
Table 1

Experiment Number	Additive	Concentration of the additive %	Coulombic efficiency %
2	$\text{CoO} \cdot \text{Al}_2\text{O}_3$	5	98
6	$\text{V}_2\text{O}_5$	5	100
9	$\text{V}_2\text{O}_5$	3	98
8	$\text{V}_2\text{O}_5$	1	97
7	$\text{NiO} \cdot \text{Co}_2\text{O}_3$	5	100
10	$\text{NiO} \cdot \text{Co}_2\text{O}_3$	3	99
11	$\text{NiO} \cdot \text{Co}_2\text{O}_3$	1	100
14	$\text{NiO}$	1	95
15	$\text{Co}_3\text{O}_4$	1	100
17	$\text{NiO} \cdot 2\text{CoO}$	1	100

For comparison to This table 1, it should be mentioned that manganese dioxide without any catalyst shows a coulombic efficiency of only 75 to 85%. The difference to 100% is given by the creation of manganese and permanganate which proportionate back to  $\text{MnO}_2$  and lower  $\text{MnO}$ -oxides. The  $\text{MnO}_2$  is again able to discharge and to be charged. The lower oxides are not rechargeable, and constitute irreversible loss.

WE CLAIM:

1. A manganese dioxide cathode for rechargeable alkaline manganese dioxide cells with improved overcharge properties, characterized by at most 10 mass% catalyst, making the oxygen evolution during overcharge stoichiometrically equivalent to the charge current without the side reaction to the managanate, said catalysts being any the following group:



2. The manganese dioxide cathode as claimed in claim 1, wherein the amount of said catalyst is between 1 and 5 mass%.
3. The manganese dioxide cathode as claimed in claim 1, comprising at most 5 mass% vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) and at most 5% nickel oxide as catalysts.
4. The manganese dioxide cathode as claimed in claim 1, comprising at most 5 mass% nickel cobaltite ( $\text{NiO} \cdot \text{Co}_2\text{O}_3$ ) and at most 5 mass% nickel oxide as catalysts.

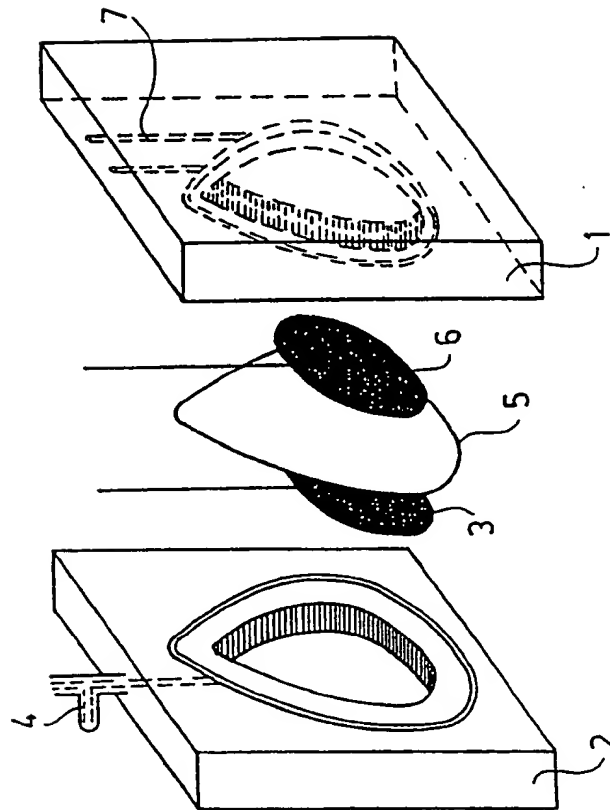


Fig.1

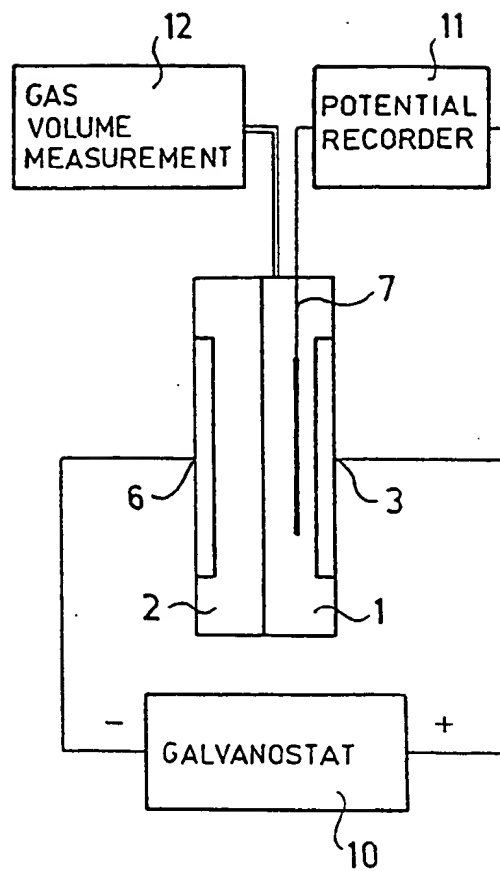


Fig. 2

3 / 11

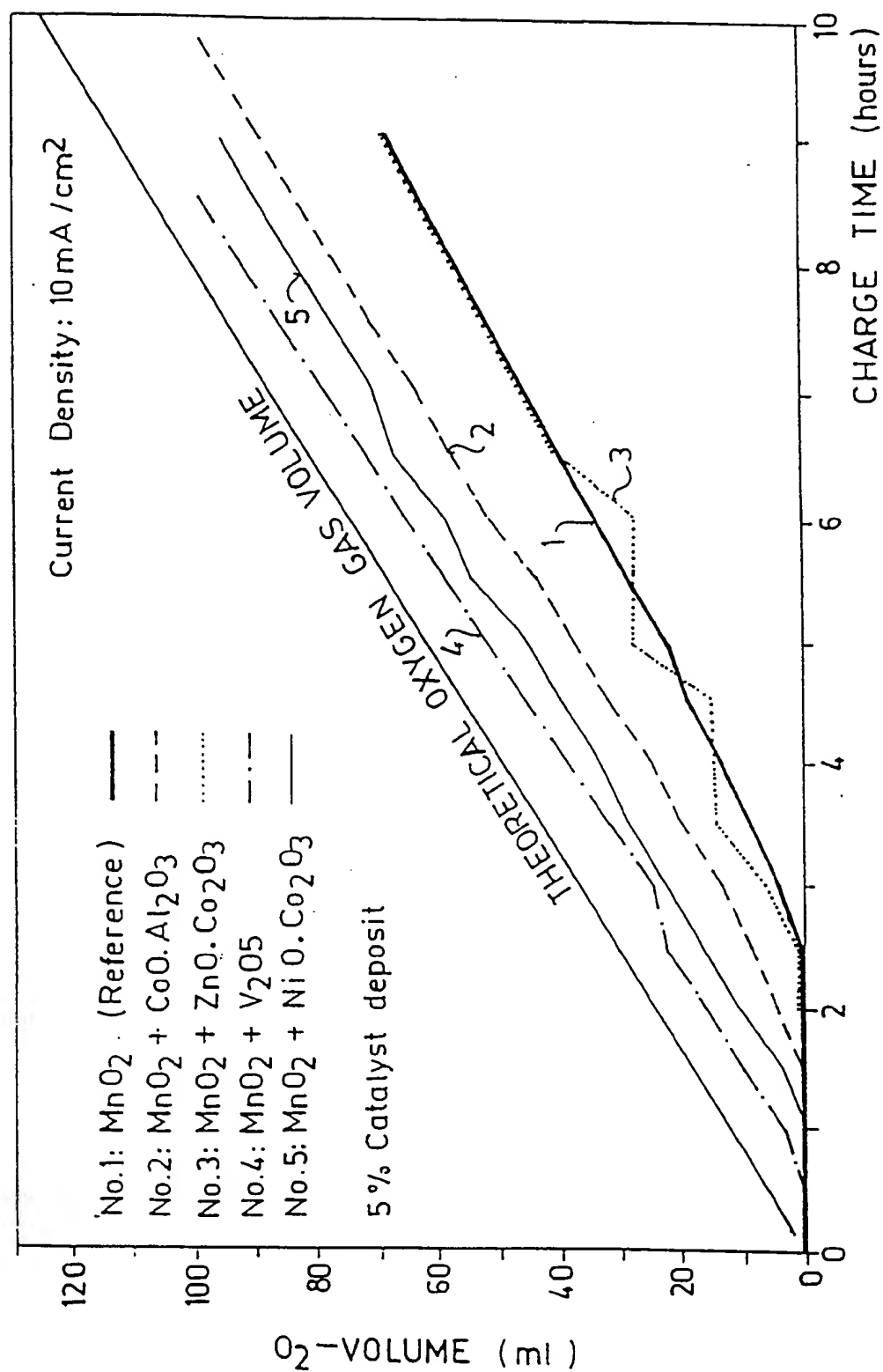


Fig.3

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4 / 11

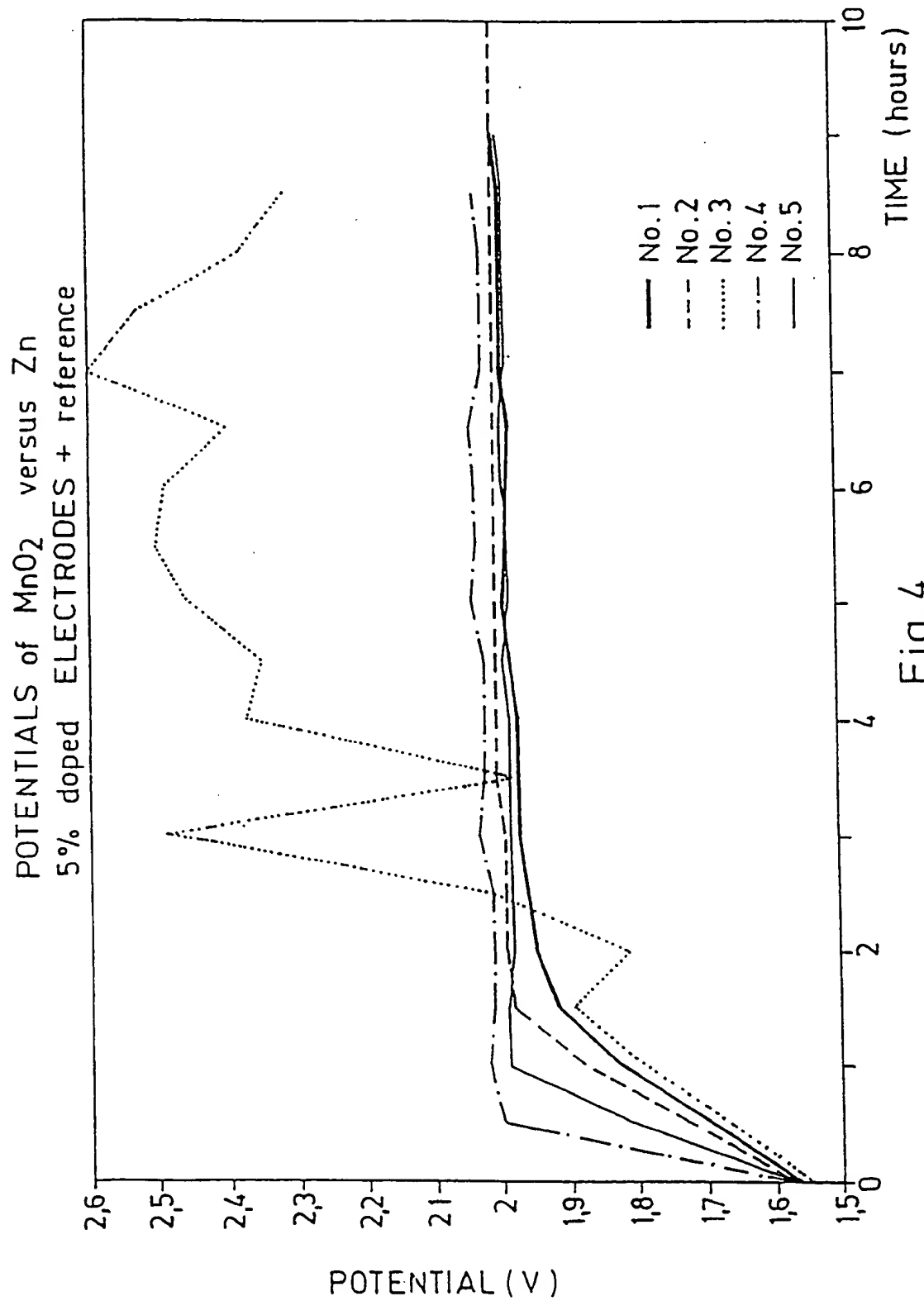


Fig.4

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5 / 11

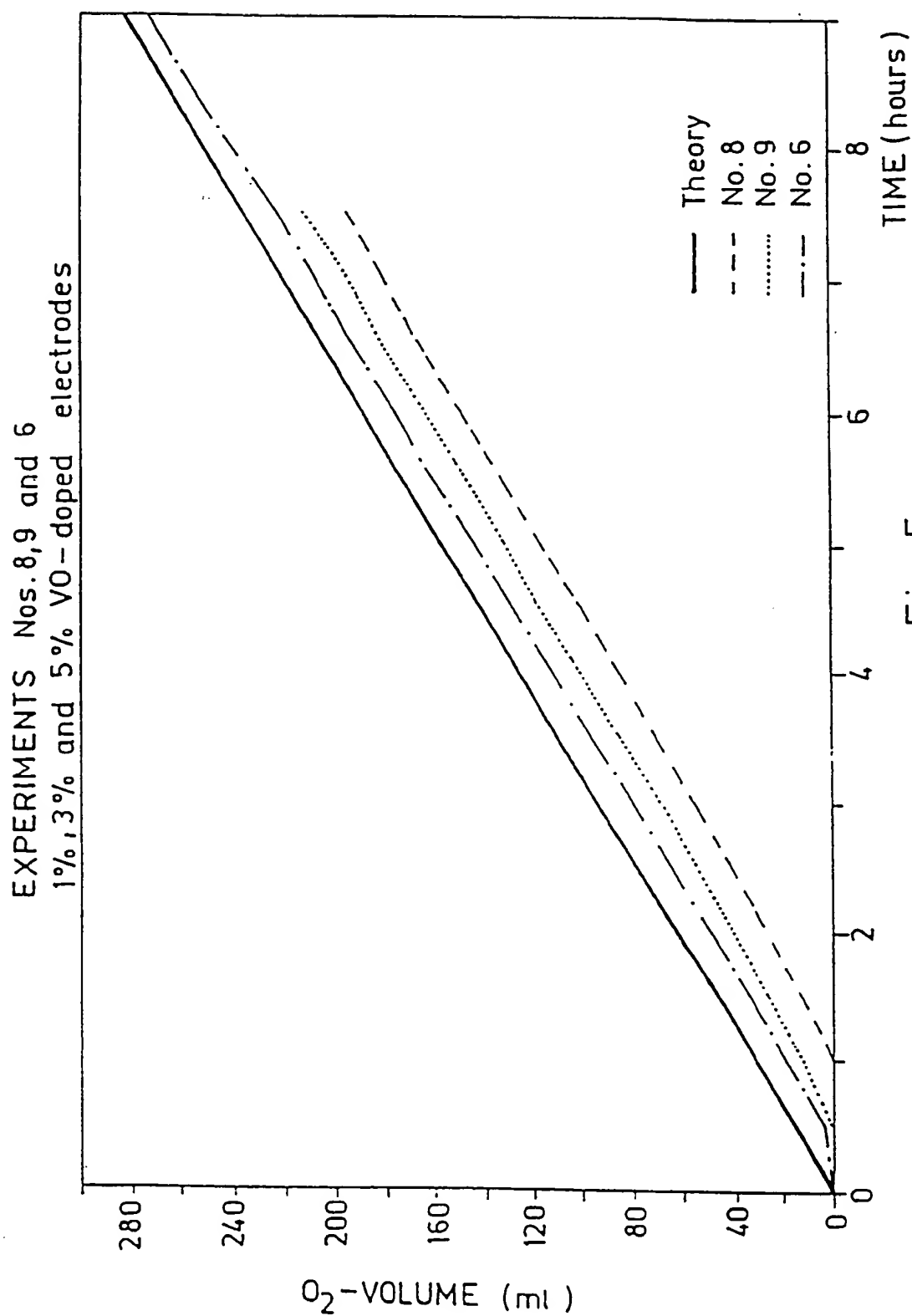


Fig. 5

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6 / 11

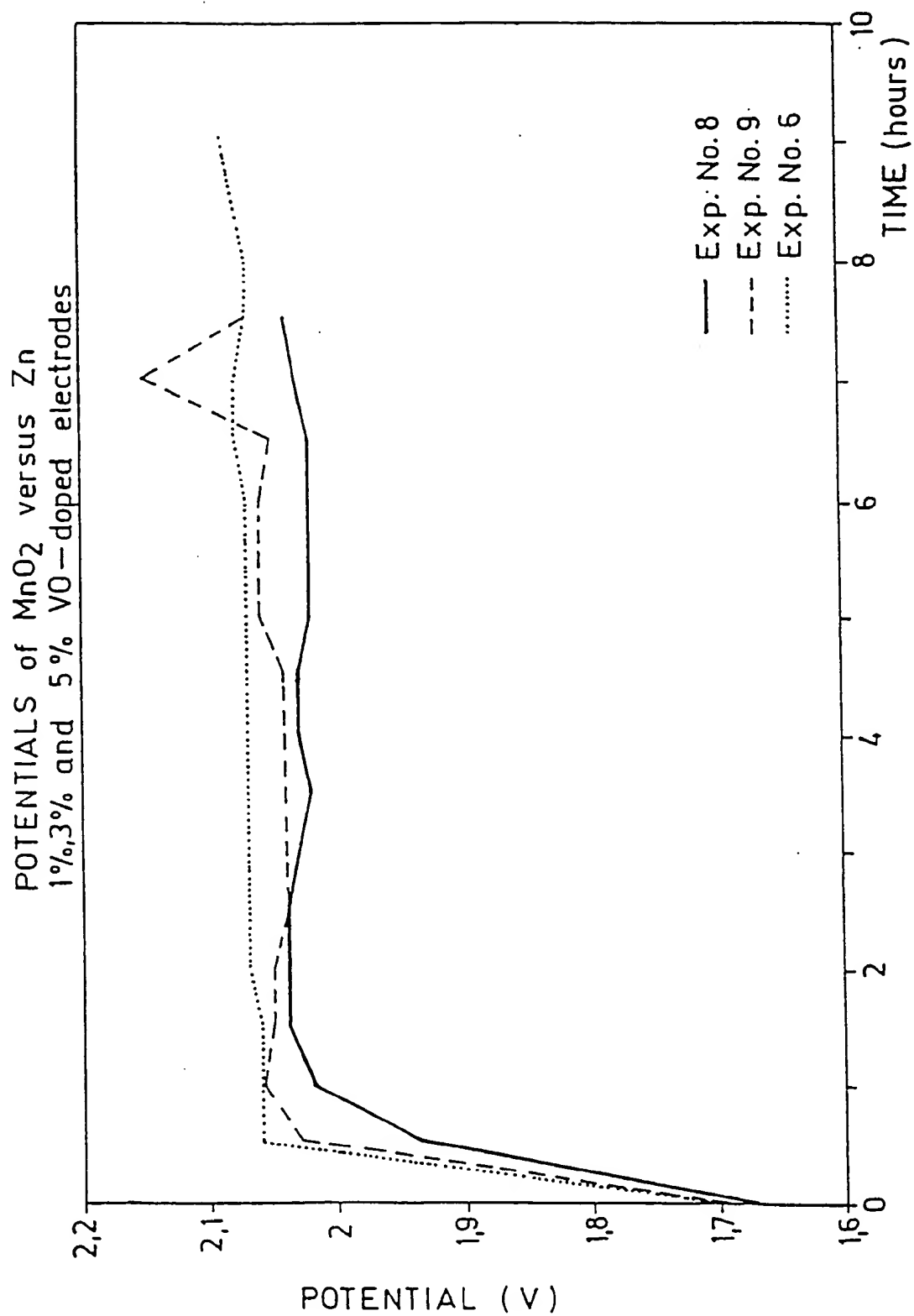


Fig.6

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7 / 11

EXPERIMENTS Nos. 11, 10 and 7  
1%, 3% and 5% NC-doped electrodes

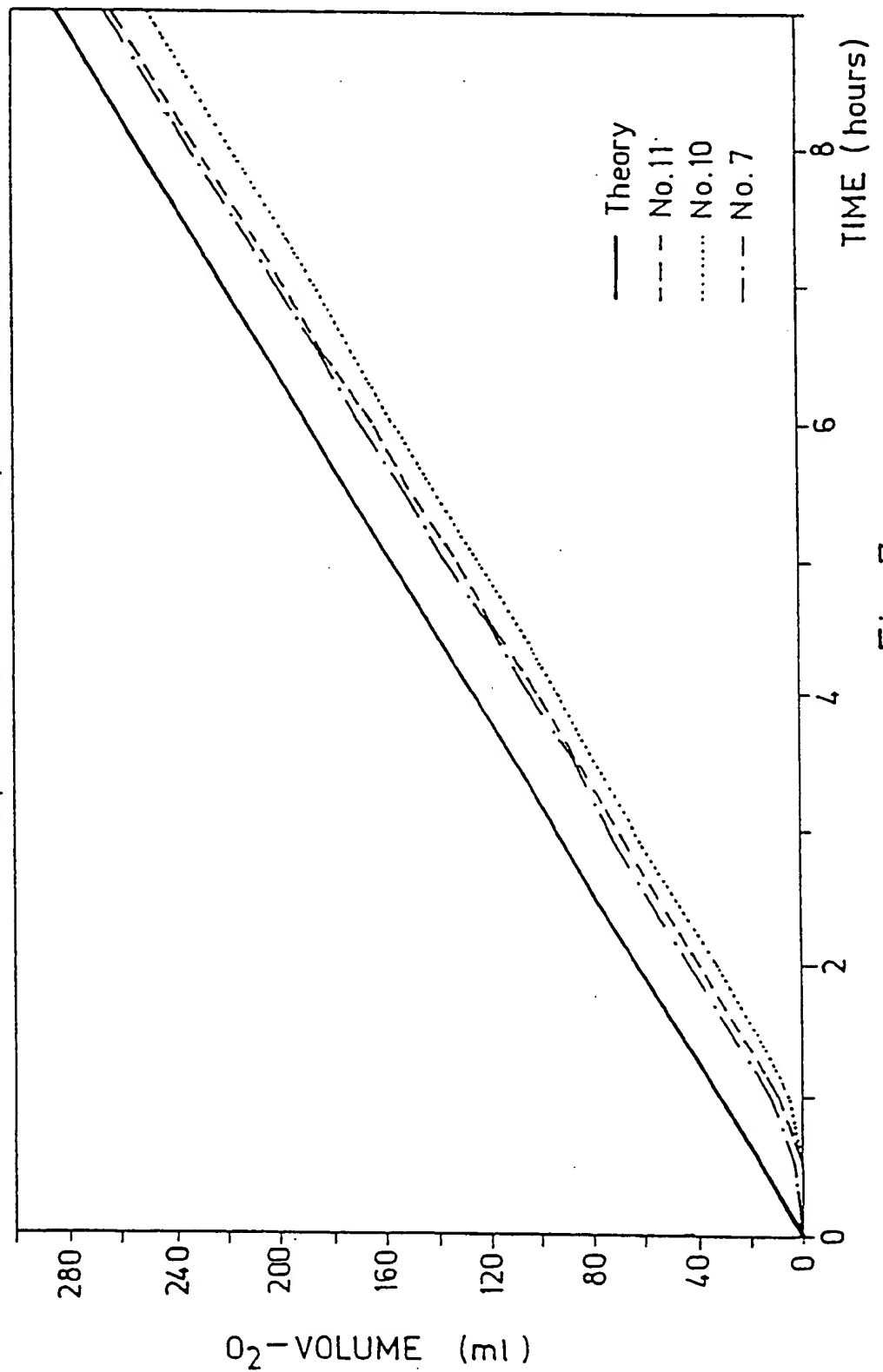


Fig. 7

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8 / 11

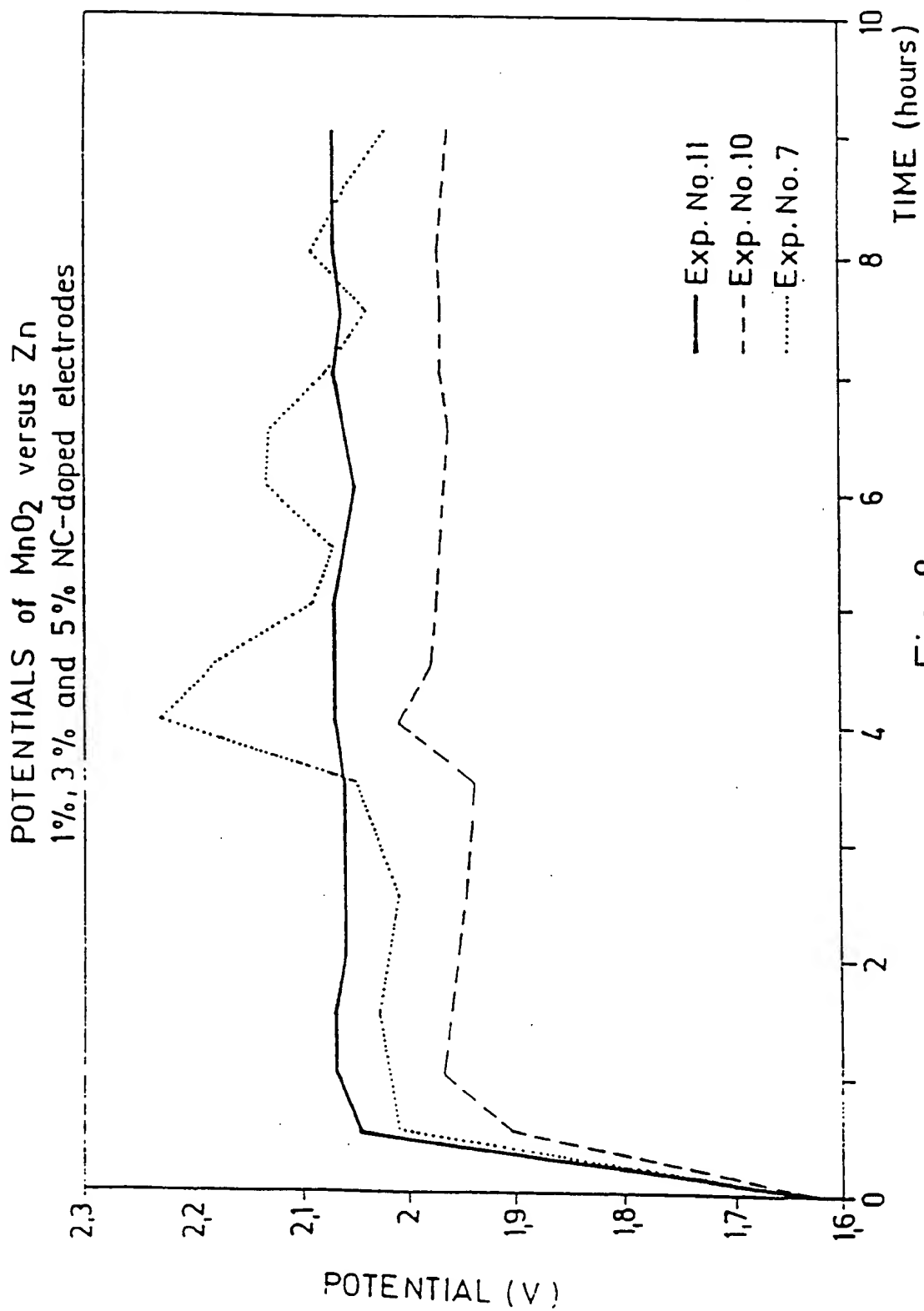


Fig. 8

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9 / 11

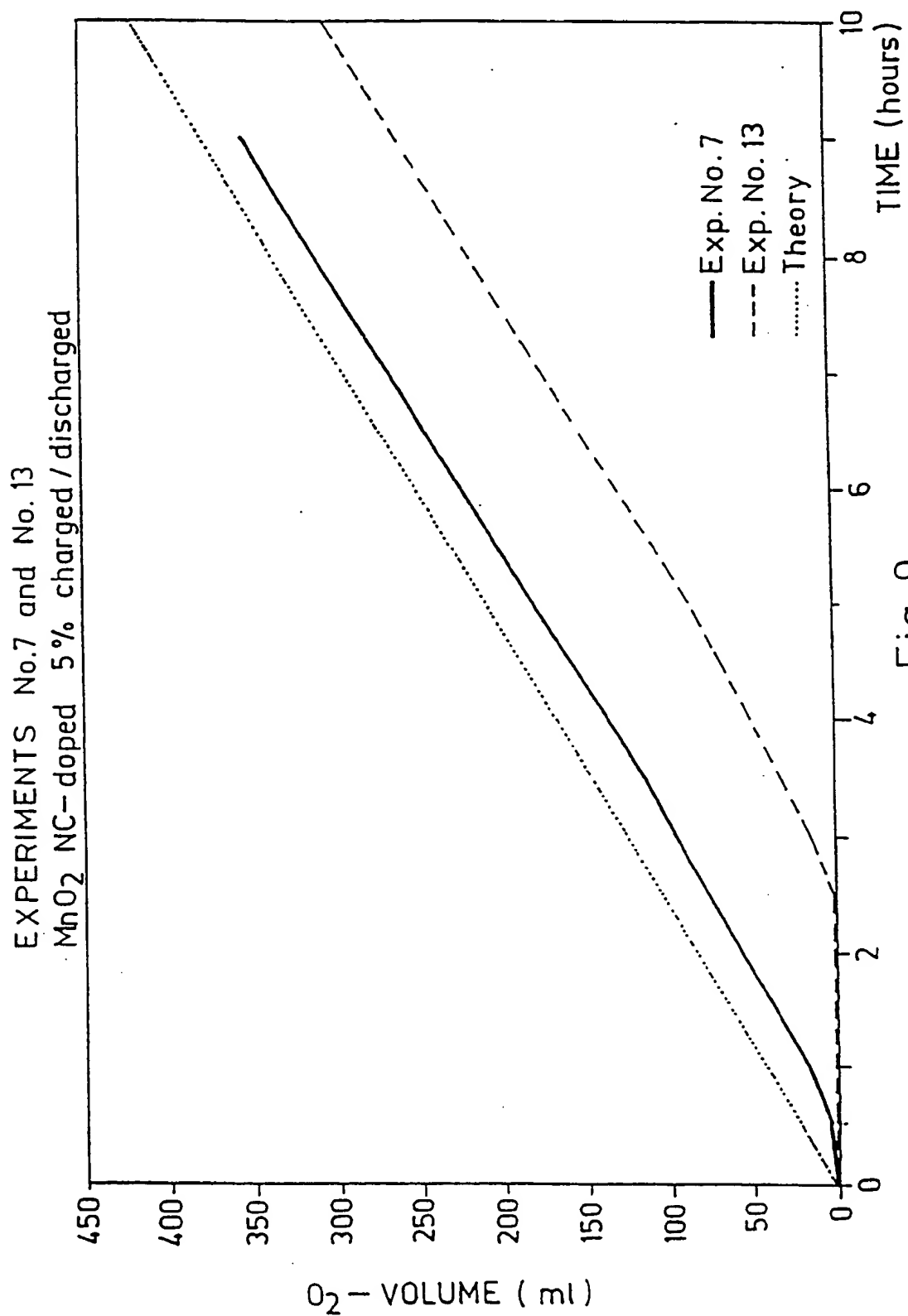


Fig. 9

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10 / 11

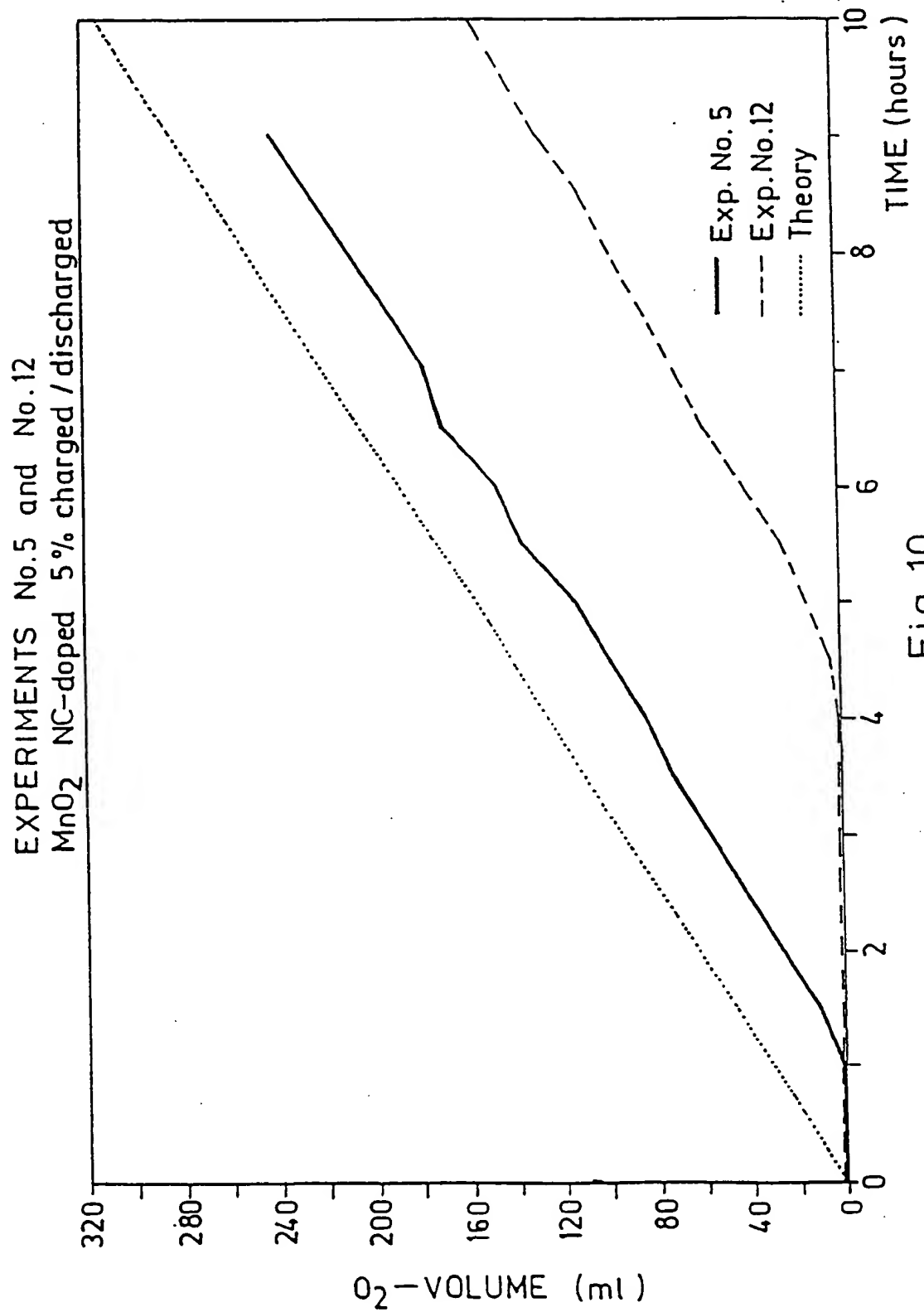


Fig.10

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11 / 11

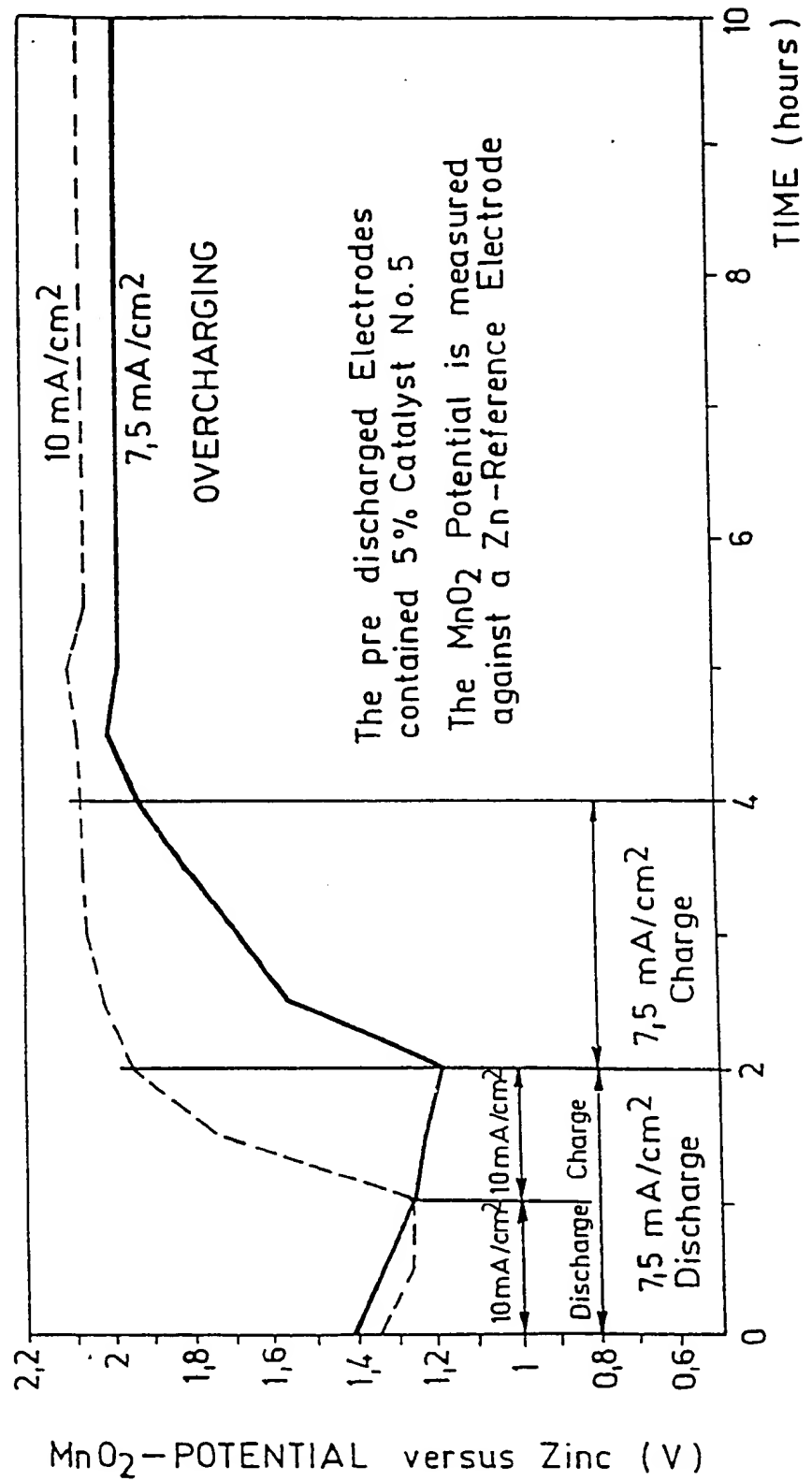


Fig.11

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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/CA 92/00140

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 H01M4/50		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	H01M	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
P,X	JOURNAL OF POWER SOURCES. vol. 36, no. 1, October 1991, LAUSANNE CH pages 45 - 56; E. KARAMAN ET AL: 'Overcharge Protection of MnO <sub>2</sub> Cathodes' see the whole document ---	1-4
X	WO,A,8 904 070 (K. TOMANTSCHGER ET AL) 5 May 1989 see claims 1,2 ---	1
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<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
21 JULY 1992	29. 07. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	ANDREWS M.P. <i>U.P. Andrews</i>	

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